

Thermotropic Biaxial Nematics: Spontaneous or Field-Stabilized?

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An intermediate nematic phase is proposed for the interpretation of recent experimental results on phase biaxiality in bent-core nematics. The phase is macroscopically uniaxial but consists of microscopic biaxial, and possibly polar, domains. On applying an electric field the phase exhibits substantial macroscopic biaxial ordering resulting from the collective alignment of the domains. A phenomenological theory is developed for the molecular order in this phase and for its transitions to purely uniaxial and to spontaneously biaxial nematic phases.

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Since their theoretical prediction, nearly four decades ago [1], biaxial nematics have been a constant challenge in liquid crystal (LC) research [2, 3, 4, 5]. They differ from the common, uniaxial, nematics in that they exhibit additional orientational order of the molecules along a second macroscopic direction, the “biaxial” or “short” axis \mathbf{m} , perpendicular to the primary nematic director \mathbf{n} . The expectation that the response of \mathbf{m} to an applied electric field could be much faster than that of \mathbf{n} has been sustaining a constant practical interest in low molecular mass biaxial thermotropic nematic LCs (i.e. the biaxial analogues of the conventional nematic LCs used in electro-optic applications). However, it was only recently that strong experimental evidence has been produced for the discovery of such biaxial nematics, first in bent-core systems [3, 4] and shortly afterwards in laterally substituted tetrapode nematogens.[5]

Subsequent electro-optic switching experiments[6] on the bent-core biaxial nematics demonstrated that the response of the \mathbf{m} axis to an applied field is indeed much faster than that of the \mathbf{n} director. Interestingly, the interpretation of these switching experiments suggests (a) the existence of a high temperature uniaxial nematic phase with practically no biaxial response to an applied electric field and (b) a transition to a low temperature nematic phase which is optically uniaxial and can be brought to a biaxial state by applying an electric field perpendicular to \mathbf{n} . As the electric field strengths involved (a few $V/\mu m$) are clearly too low to produce a substantial effect directly on the orientations of individual molecules, the field-induced biaxial state is attributed to the preferential alignment of the \mathbf{m} axes of pre-existing biaxial molecular aggregates (domains or clusters) which, in the absence of an applied field, are randomly distributed about \mathbf{n} . Electric fields of similar strength have been used to switch the \mathbf{m} director in the XRD experiments of ref[4].

The spinning-sample NMR experiments in ref[3] do not involve electric fields but there, the strong external magnetic field, when not collinear with the \mathbf{n} director, would orient the \mathbf{m} axis (here identified with the direction of smallest diamagnetic susceptibility of the phase) perpendicular to the plane formed by \mathbf{n} and the field direc-

tion. Consequently, it is possible that the static sample consists of biaxial domains with their \mathbf{m} axes randomly distributed about a common \mathbf{n} director (parallel to the magnetic field) and that a macroscopic alignment of the domain \mathbf{m} axes results from spinning the sample about an axis perpendicular to the magnetic field.

Recent atomistic simulations of nematics made of bent-core molecules[7] indicate the existence of biaxial domains. In general, such domains exhibit dielectric as well as diamagnetic biaxiality and would therefore be readily oriented by external fields. In fact, the domains found in ref [7] exhibit local ferroelectric (i.e. biaxial and polar) nematic ordering. This endows the domains with a net electric polarisation which could also orient them macroscopically in an external field. Dielectric fluctuation studies by dynamic light scattering in the uniaxial nematic phase of bent-core liquid crystals suggest the formation of cybotactic (smectic-like) clusters [8] and, in one instance [9], randomly oriented nanodomains of antclinic ferroelectric smectic ordering are proposed for the structure of an optically isotropic phase obtained on cooling from the nematic phase. Lastly, persistent cybotactic biaxial clusters are clearly identified in XRD studies of calamitic multipode nematics for which the low temperature phases are columnar [10]. These considerations suggest that the existence of uniaxial phases both, with and without biaxial clusters, and the possibility of field-induced alignment of the latter, might be of key relevance to the understanding of phase biaxiality in thermotropic nematics.

An alternative way to view the aligning effect of the external field is in terms of the orientational fluctuations of \mathbf{m} . The hypothesis that these fluctuations are extensive enough to destroy the spontaneous long-range alignment of the \mathbf{m} axis has been often used [2] as a possible explanation of why, in spite of the predictions from molecular theory, thermotropic biaxial nematics are not commonly observed in experiments. On the other hand, in analogy with what is known from the elastic continuum theory of uniaxial nematics [11], the application of an external field would quench the low wave-vector orientational fluctuation modes of the \mathbf{m} axis. Thus, a possible interpretation

of the observed field-induced transition to a biaxial state is through the quenching of the low-energy orientational fluctuation modes. However, estimates of cluster sizes and time scales of their reorientational motions indicate that a continuum treatment of the biaxial fluctuations may not be applicable.

In any case, the conventional static formulation of the nematic phase free energy solely in terms of long range orientational order parameters refers to a single-domain, uniformly ordered system and can therefore convey neither the cluster picture nor the continuum fluctuation picture of the field-induced transition to the biaxial state. In this letter we introduce a phenomenological description that allows explicitly for non-uniformity of the biaxial orientational order in a thermotropic nematic phase. The formulation is based on the biaxial cluster picture, allowing for a full range of cluster sizes, from single molecule to macroscopic aggregates, thus avoiding the inherent size-limitations of a continuum treatment.

To identify the relevant order parameters in a phase with local biaxial nematic order we consider a nematic sample of N molecules in a volume V at temperature T with the director \mathbf{n} perfectly aligned along the Z macroscopic axis. Practically, the sample may be pictured as filling the space between parallel plates, with the Z axis defining the rubbing direction that aligns the director \mathbf{n} on the plate surfaces. The X macroscopic axis is taken to lie on the plane of the plates and the Y to be perpendicular to that plane. For simplicity we further assume that the molecules are themselves perfectly aligned with their major axis z parallel to the primary director \mathbf{n} . This restricts the local biaxial \mathbf{m} axis as well as the molecular axes x, y on the plane defined by the macroscopic X, Y axes. We also assume that the sample-confining surfaces have no aligning influence on the \mathbf{m} axis. We then assign to each molecule a traceless second rank molecular tensor m_{ab} which in the principal molecular frame of axes $\{a, b\} = x, y, z$ may be taken to have the components $-m_{xx} = m = m_{yy}$ and $m_{zz} = 0$. Next, assuming that the sample is divided into a number R ($\leq N$) of clusters, each labeled by an index r and containing n_r molecules, we may define for each such cluster a tensor

$$M_{A_r B_r}^{(r)} = \sum_{i=1}^{n_r} m_{A_r B_r}^{(i)} \quad , \quad (1)$$

where A_r, B_r denote the principal axes in the cluster r and the index i runs over all the molecules in that cluster. The cluster tensor will thus have two non-vanishing principal components; these can be expressed in terms of a single quantity $M^{(r)} = -M_{X_r X_r}^{(r)} = M_{Y_r Y_r}^{(r)}$. Obviously $M^{(r)}$ depends both on the size of the cluster, through the number n_r of the molecules it comprises, and on the degree of biaxial ordering of these molecules. The short \mathbf{m}_r axis of the cluster is taken to coincide with one of he principal axes, say Y_r .

The rotational invariants associated with the molecular and the cluster tensors are respectively $m_{ab}m_{ab} = 2m^2$ and $M_{A_r B_r}^{(r)} M_{A_r B_r}^{(r)} = 2(M^{(r)})^2$ (summation over repeated tensor indices is implied). By summing the individual invariants of all the clusters one may define the following invariant quantity for each possible partitioning $\{r\}$ of the sample into clusters:

$$\sigma\{r\} = \frac{1}{m^2(N^2 - 1)} \sum_{r=1}^R \left[(M^{(r)})^2 - m^2 \right] \quad (2)$$

This quantity strictly vanishes if each cluster contains a single molecule, it reduces to $\sigma\{r\} = -1/(N^2 - 1) \approx 0$ if all the clusters have vanishing $M^{(r)}$ (i.e. if they are uniaxial) and it takes the highest possible value $\sigma\{r\} = 1$ if the sample consists of a single cluster containing all the N mesogens with their molecular axes x, y perfectly aligned along the macroscopic directions X, Y respectively. Denoting by $\sigma\{\tilde{r}\}$ the largest value that can be obtained for any of the different possible ways of partitioning the sample into clusters in a given microstate, one may define the cluster order parameter σ as the ensemble average $\sigma \equiv \langle \sigma\{\tilde{r}\} \rangle$. This parameter varies in the range $0 \leq \sigma \leq 1$ and gives the extent of biaxial ordering within the clusters but does not give a direct measure of long-range biaxiality. To describe the latter we use the following macroscopic, second rank and traceless, tensor in its principal axis frame $A, B = X, Y, Z$,

$$q_{AB} = \frac{1}{Nm} \left\langle \sum_{r=1}^R M_{AB}^{(r)} \right\rangle \quad , \quad (3)$$

with principal values $-q_{XX} = q_{YY} = q$, and $|q| \leq 1$. The quantity q measures the extent of phase biaxiality. In the absence of an external field, this biaxiality is understood to originate from the spontaneous collective alignment of the clusters short axes \mathbf{m}_r .

Due to the assumed restriction of the molecular z -axis along the macroscopic Z direction, the invariants that can be formed from the biaxiality tensor q_{AB} are even powers of q (i.e. $q_{AB}q_{AB} = 2q^2$, $q_{AB}q_{BC}q_{CA} = 0$ etc). The electrostatic interaction of the biaxial medium with an applied electric field, taken to have components $E_Y = E$, $E_X = E_Z = 0$, is conveyed, to lowest order in q by a term $hE_A E_B q_{AB} = hE^2 q$, where the scalar factor h reflects the magnitude of the molecular polarisability anisotropy in the x, y molecular plane. Accordingly, the leading terms in a phenomenological Landau-deGennes expansion of the free energy in terms of the order parameters σ and q will be

$$F = a\sigma + \frac{b}{2}\sigma^2 + \frac{g}{3}\sigma^3 + \frac{c}{2}q^2 + \frac{d}{4}q^4 - e\sigma q^2 - hE^2 q \quad (4)$$

Considering σ as the primary order parameter, the coefficient a is taken to be an increasing function of the temperature, exhibiting a rapid variation in the vicinity

of a characteristic temperature T_0 at which it changes sign. The other coefficients b, c, d, e, h, g are all assumed to be insensitive to variations of temperature and positive, with the exception of b , for which both signs are considered. The c and d terms correspond to the entropic drop caused by the ordering and the e term is the energetic contribution associated with the coupling between the local ordering of the individual clusters (σ) and their collective ordering (q).

With no applied field ($E = 0$), the free energy in eq (4) describes three possible nematic phases: (i) a “proper” nematic phase (N_u), in which $\sigma = q = 0$; (ii) a macroscopically uniaxial nematic phase ($N_u^{(bc)}$) formed by randomly oriented biaxial clusters, in which $\sigma > 0$ and $q = 0$; (iii) a macroscopically biaxial phase ($N_b^{(bc)}$) formed by ordered biaxial clusters, in which $\sigma > 0$ and $q \neq 0$. Representative order parameter profiles for these phases, and the possible phase transition sequences are depicted in Fig. (1).

For $b < 0$, the transition from the N_u to the $N_u^{(bc)}$ phase is of first order, Fig. (1a), and is obtained when a reaches the value $a^* (= 3b^2/(16g))$, at which point the cluster order parameter undergoes a jump from $\sigma = 0$ to $\sigma = \sigma^* (= 3|b|/(4g))$. A further transition from the $N_u^{(bc)}$ to the $N_b^{(bc)}$, which is of second order, is obtained in this case as σ increases beyond a critical value $\sigma_c (= c/(2e))$, provided that the ratio $\lambda = \sigma_c/\sigma^*$ is $\lambda > 1$. The respective value of a at this transition is $a_c = a^*\lambda(4 - 3\lambda)$. If $\lambda < 1$, the $N_u^{(bc)}$ phase is removed from the sequence, Fig. (1b), and a direct, first order, N_u to $N_b^{(bc)}$ phase transition is obtained at $a = a_d (< a^*)$, with both σ and q rising abruptly from 0 to finite values σ_d and q_d .

For $b > 0$ the transition from the N_u to the $N_u^{(bc)}$ phase is of second order, Fig. (1c,d), at $a = 0$ and is followed by a transition from the $N_u^{(bc)}$ to the $N_b^{(bc)}$ on lowering a to the value $a^\dagger = -a^*\lambda(4 + 3\lambda)$. The order of this transition is controlled by the parameters λ and $u (= 2e^2/(|b|d))$, with $u < 1 + 3\lambda/2$ defining the range of the second order phase transition.

In the presence of an electric field ($E \neq 0$) the uniaxial phases N_u and $N_u^{(bc)}$ acquire field-induced biaxiality, to which we now focus our attention, particularly for the case $b < 0$ and $\lambda > 1$ which is directly relevant to the biaxial electro-optic response and the nematic-nematic phase transitions observed experimentally in bent-core nematics[6].

The dependence of the order parameters σ and q on the temperature function a is shown in Fig. 2 for different magnitudes of the applied electric field. It is apparent from the plots of the biaxiality order parameter $q(a, E)$ that the effect of the electric field is much stronger in the $N_u^{(bc)}$ phase, where the biaxial ordering is produced by the alignment of the biaxial clusters, compared to the N_u phase where the field influences directly the orientations

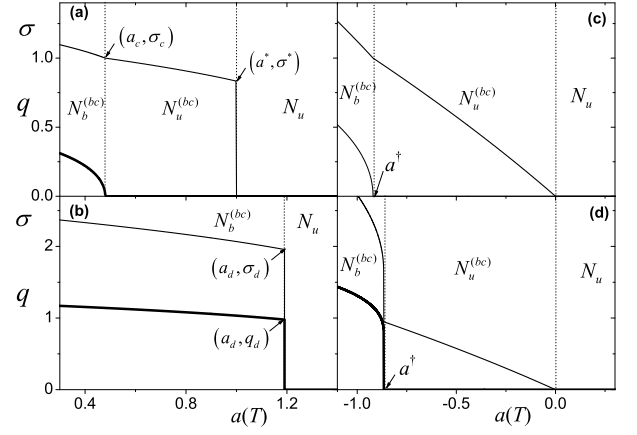


FIG. 1: Plots of the temperature dependence of the calculated order parameters for four representative combinations of the values of the expansion coefficients in eq (4): (a) $b < 0$, $\lambda = 1.2$, $u = 0.5$. (b) $b < 0$, $\lambda = 0.7$, $u = 0.5$. (c) $b > 0$, $\lambda = 0.2$, $u = 1.5$. (d) as for (c) with $u = 0.5$. The cluster order parameter σ (thin lines) is expressed in units of σ_c , the biaxiality order parameter q (thick lines) is expressed in units of $\sqrt{c/d}$. The temperature function $a(T)$ is scaled by the constant $a^* = 3b^2/16g$.

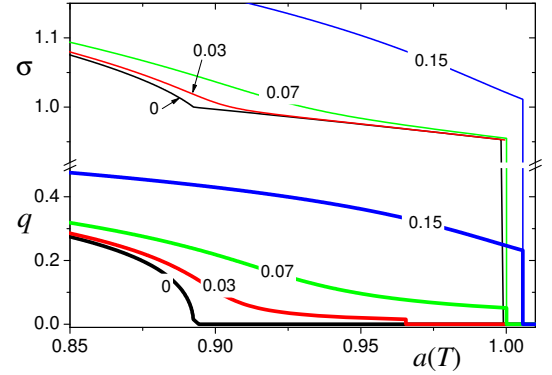


FIG. 2: Temperature dependence plots of the calculated order parameters σ (thin lines) and q (thick lines) for $b < 0$, $\lambda = 1.05$, $u = 0.5$, for the indicated values of the applied electric field E , expressed in units of $(a^*c^2/2eh^2)^{-1/4}$.

of the molecules. At constant E , the transition from N_u to $N_u^{(bc)}$ is accompanied by a jump in q that is proportional to E^2 . A phase transition of this type, reflected on the abrupt change in the biaxial response of a uniaxial nematic phase to an applied electric field, has been observed by J-H Lee *et al.*[6].

For weak applied fields, a measure the susceptibility of the system to field-induced biaxial ordering is provided by the “electro-biaxial” coefficient $k \equiv \frac{\partial q}{\partial E^2} \Big|_{E=0}$. In the N_u phase, the value of this coefficient is fixed to $k_{N_u} = h/c$, while in the $N_u^{(bc)}$ phase it varies with σ (and therefore with temperature) according to $k_{N_u^{(bc)}} = (h/c)(1 - \sigma/\sigma_c)^{-1}$. Thus, at the transition the electro-

biaxial susceptibility undergoes a jump of $h/(c(\lambda - 1))$. This can be quite large in systems for which the λ ratio is close to one. In this case a weak field could induce considerable biaxial order to a uniaxial nematic phase.

The results regarding the application of an electric field should be viewed within the practical limitations that the assumed alignment of the director \mathbf{n} imposes on the possible magnitude of the applied field E : To actually maintain the uniform orientation of \mathbf{n} along the rubbing direction (Z axis) of the plates for a nematic of positive dielectric anisotropy, the field strength cannot exceed the critical value E_c for the Fredericzs transition that reorients \mathbf{n} along the Y axis. Apparently, no such limitation applies for nematics of negative dielectric anisotropy; in this respect, such systems would be advantageous for the study of electric field-induced biaxial order in the $N_u^{(bc)}$ phase.

To summarise the results, three nematic phases are identified in the absence of an applied field: a purely uniaxial phase, a spontaneously biaxial phase and an intermediate, macroscopically uniaxial phase consisting of biaxial clusters that are randomly oriented. The application of an electric field could induce substantial biaxial order to this intermediate ($N_u^{(bc)}$) phase. The switching of this phase between an optically uniaxial and a biaxial state as well as its possible transformation to a nematic phase (N_u) in which the application of a weak or moderate electric field does not induce a measurable optical biaxiality, are in agreement with experimental observations on bent-core nematics[6].

The above properties of the $N_u^{(bc)}$ phase are not in contradiction with the experimental observations of biaxiality by NMR[3] and XRD [4] since in both cases an aligning field, magnetic or electric, is present. Furthermore, according to the induced nature of biaxiality suggested by the present analysis, the measured values of the biaxial order parameter by the two experimental methods should in general differ, as in fact they do, because the biaxiality-inducing fields and mechanisms are different in the two methods. It is also worth noting that the emergence of macroscopic biaxial nematic ordering from the collective alignment (spontaneous or field induced) of clusters is supported by the experimental observation of biaxial order in nematic tetrapodes[5]. Here, the covalent lateral grouping of the nematogen components into quartets promotes the clustering which, in turn, enhances the biaxial tendency relative to that of the non-bonded nematogens.

The free energy expression in eq (4) can be readily extended to include the possibility of polar ordering within the biaxial clusters. In close analogy with the formulation of the σ parameter a parameter, ρ is introduced to describe the average magnitude of polar ordering within the clusters in a direction transverse to \mathbf{n} . The net transverse polarity of the sample is quantified by means of a vector order parameter p_A that couples linearly ($p_A E_A$)

to the applied field and quadratically ($p_A p_B q_{AB}$) to the biaxial order parameter q . The additional phases described by the extended Landau- deGennes expansion include a macroscopically uniaxial nematic phase of biaxial and polar clusters, $N_u^{(pbc)}$, and a polar-biaxial nematic phase $N_{pb}^{(pbc)}$. Details on the possible phase transitions and field-induced effects are presented in a forthcoming publication.

All the results discussed here are based on a simplified formulation of the theory wherein perfect uniaxial nematic order is assumed and therefore molecular rotations are restricted in two dimensions. As a result, any dependence on the degree of uniaxial nematic ordering is suppressed. Removal of this restriction makes the formulation more elaborate and modifies the details of the phase transitions. However, the essential findings regarding field-induced biaxiality and polar ordering are preserved. These findings offer new insights into the nature of phase biaxiality and the related nematic-nematic phase transitions and broaden the current views on what could be considered as a “biaxial nematic” LC for the purposes of electro-optic device applications. In particular, the possibility that some of the known uniaxial nematics could in fact consist of randomly distributed biaxial clusters, suggests that it might be interesting to study more closely the electro-optics of certain “uniaxial” nematics, specially those with negative dielectric anisotropy. As the possibility of fast, field-induced, switching between uniaxial and biaxial (and possibly polar) states provides a new concept for the design biaxial nematic devices, such studies might also be of practical importance.

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